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BSTRACT (*Maximum 200 words*)

The instrumentation acquired from this grant consists of two atomic force microscopes (from Park Scientific and Molecular Imaging) and a particle size analyzer (from Micromeritics). The atomic force microscopes are complementary in terms of their operation and use the same controller and software. The Park Scientific instrument has been used to characterize the microstructure development of thin films of the oxygen ion conductor, BICUVOX ($Bi_2V_{0.9}Cu_{0.1}O_{5.35}$) over the temperature range from 550 to 800°C. Grain growth occurring in the film appears to be two-dimensional in nature. The Molecular Imaging AFM is designed for characterizing the topology of liquid-solid interfaces. This instrument has been used to image the surface of a lithium battery cathode material, V_2O_5, during lithium intercalation. The particle size analyzer has been used to characterize the particle size and particle size distribution of powders of various materials produced by the Pechini method as a function of heat treatment temperature.

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Air Force Office of Scientific Research

FINAL TECHNICAL REPORT

for

Grant Number: F49620-96-1-0474

Oxygen Ion Conductors Prepared with Nanosize Particles

Project Period: 15 September 1996 to 14 September 1997

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DESCRIPTION OF ACQUIRED EQUIPMENT

The equipment purchased by this grant is as follows:

1) Atomic Force Microscopes

a) AutoProbe - Scanning Probe Microscope System

(Park Scientific Model AP - 0190; Compact Probe System)

Additional features: On-axis optical microscope, electronics module with materials analysis software package, vibration isolation package

Manufacturer: Park Scientific Instruments
1171 Borregas Avenue
Sunnyvale, CA 94089

b) Pico Scanning Probe Microscope

(Molecular Imaging Model AFM 300)

Additional features: potentiostat for electrochemical operation, environmental chamber, liquid measurement cell.

Manufacturer: Molecular Imaging Corp.
9830 S. 51st St.
Phoenix, AZ 85044

2) Partical Size Analyzer

Micromeritics - Sedigraph Model 5100

Manufacturer: Micromeritics
1 Micromeritics Drive
Norcross, GA 30093

EQUIPMENT USE

The instruments acquired from this grant consist of two Atomic Force Microscopes (AFMs) and a particle size analyzer. The AFMs, both of which may be used at ambient atmosphere, are complementary in their usage. These instruments are based on measuring the deflection of a soft force sensing cantilever as a probe tip is scanned over a surface. Minute deflections are sensed by an optical sensor. Vertical deflections of the cantilever are converted to angular deflections of a laser beam reflected from the end of the cantilever. The displacment as a function of position on the surface is mapped onto a display to provide a quasi-three dimensional representation of the surface topology. The Park

Scientific AFM has been used for characterizing the surface topology of thin films of oxygen ion conducting ceramics. The AFM from Molecular Imaging is designed for characterizing the topology of liquid-solid interfaces of the type which occur in electrochemical devices. We have used it to characterize the dimensional changes occurring during the operation of secondary lithium battery cathode materials. The AFMs were purchased as a "package" because both operate from the Park Scientific controller and software. Both AFMs possess a wide range of capabilities which enable us to visualize the microstructure of thin films at the sub-nanometer level and to provide quantitative information concerning the morphology, grain size, thickness and roughness of thin films.

The particle size analyzer provides quantitative information concerning the particle size distribution of ceramic powders over the range 200 μm to 0.1 μm. The instrument is based on the use of X-ray absorption and requires that the particles be well suspended in an appropriate liquid. We have used the sedigraph to determine the change in particle size of $LiCoO_2$ powders as a function of heat treatment.

Selected research projects which used the acquired instruments are described below.

a. Characterization of BICUVOX Thin Films

This work concerned the preparation of oxygen ion conducting thin film ceramics based on the bismuth vanadate ($Bi_4V_2O_{11}$) family of compositions. These materials are presently the most promising oxygen ion conducting solids in the temperature range of 200-600°C. Of these, the highest conductivities have been exhibited by copper substituted bismuth vanadates (so called BICUVOX), in particular for a copper substitution of 0.1 moles for vanadium ($Bi_2V_{0.9}Cu_{0.1}O_{5.35}$). Our previous work on this material confirms that its oxygen ion conductivity at 400°C (typically 2×10^{-2} S/cm) is some 50 times greater than any other solid electrolyte in this temperature range. In our current research program, we are developing methods of synthesizing thin films of this composition for electrochemical oxygen pump applications. Thin films are required in order to reduce the resistive losses which occur in the electrochemical device.

BICUVOX thin films were prepared by spin coating metal-organic precursor solutions (corresponding to the desired BICUVOX composition) onto MgO substrates at room temperature. Subsequent pyrolysis of these films at temperatures above 500°C yielded the desired BICUVOX phase. The thickness of a single spun film after pyrolysis was in the range of 200-400 nm. To produce films of greater thickness, a multi-layer process was employed whereby additional organic precursor films were spun on top of the

pyrolyzed BICUVOX film. Applying 10 films produced a final film thickness of 2-4 μm. This is the range of thickness required for oxygen pump applications.

A fundamental part of our work on BICUVOX thin film processing involved studying microstructure development as a function of the sintering temperature of the films. Initially this was conducted using scanning electron microscopy (SEM). However, SEM is limited due to the fact that it requires the BICUVOX samples under observation to be coated with a thin layer of gold or carbon to ensure that the sample is sufficiently conductive for microscopy. This process essentially destroys the sample and prevents one from observing the effects of successive processing treatments on a given sample. The AFM requires no such coating procedure and allows a single sample to be investigated over the complete range of sintering temperatures concerned. In our experiments, a sample was heated to 550°C and, after cooling, examined using the AFM. Following the AFM analysis, the same sample was reheated to 650°C, similarly examined and so on. Figure 1 shows AFM micrographs indicating grain growth in the BICUVOX thin film over the temperature range 550°C to 800°C. As expected, higher sintering temperatures yield larger grain sizes. However, it is interesting to note that the grain size of the films is significantly greater than the thickness of the film. The film in Figure 1 is approximately 200 nm thick. This suggests that the grain growth is 2-dimensional in nature. At some point the grains become larger than the thickness of the film and must grow 2-dimensionally in order to produce the structure observed. The AFM also enables us to visualize the effects of the multi-layering process on the resulting microstructure.

This project was supported by the AFOSR (Grant: F49620-95-1-0175). A manuscript on the synthesis of thin films has been accepted for publication in the *Journal of Materials Research.* The AFM study is part of continuing research.

b. Imaging of Lithium Intercalation in Vanadium Oxide

There is considerable interest in the use of V_2O_5 as a cathode material for secondary lithium batteries. A critical feature for this material is the reversible intercalation of Li^+ within the $V_2O_5 \cdot nH_2O$ xerogel network. The issues of local chemistry and structure are certain to be important factors in determining the electrochemical properties of these materials. TEM studies have shown that $V_2O_5 \cdot nH_2O$ gels are composed of ribbon-like fibers, however, there have yet to be studies of how these ribbons pack in the solid state and how Li^+ intercalation affects this packing. We are presently using AFM to visualize the topological changes which occur in V_2O_5 during electrochemical cycling.

The studies use the Molecular Imaging instrument (PicoSPM) because it has been designed for performing liquid AFM. Unlike the Park Scientific AFM scanner, the

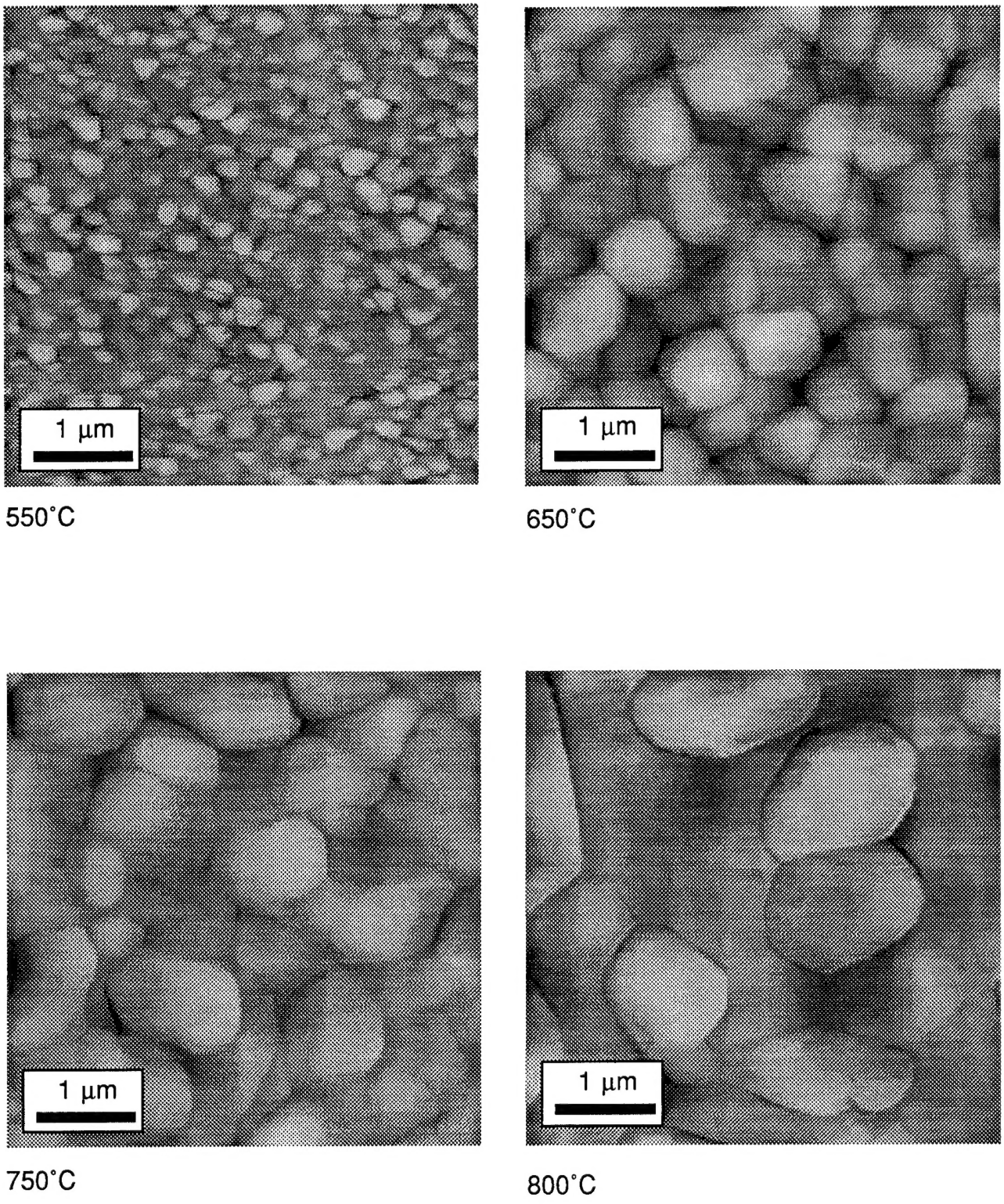

Figure 1. AFM images indicating grain growth effects in BICUVOX.10 thin films with temperature

PicoSPM is a top actuated scanner making loading and operation of liquid electrolyte, electrochemical cells possible. A three electrode cell, consisting of a vanadium pentoxide (V_2O_5) xerogel as the working electrode, with lithium counter and reference electrodes and an organic electrolyte (1 M $LiClO_4$ in propylene carbonate), is currently being tested. Because of the reactivity of this system, the PicoSPM is placed in an argon-filled glove box. In-situ cyclic voltammetry and complex impedance measurements are made while scanning the thin-film V_2O_5 cathode surface.

Our experiments involve imaging the surface of the V_2O_5 intercalation compound during the lithium intercalation/deintercalation (i.e., cell discharge and charge) processes. From these studies we will be able to correlate topological changes with interfacial reactions (as determined from complex impedance) and electrochemical behavior. An example of how the surface morphology of the V_2O_5 gel changes during galvanostatic discharge is shown in Figure 2. Three AFM images were taken during the discharge process at decreasing potentials (2.44 V, 2.17 V and 1.80 V) and correspond to increasing amounts of intercalated lithium. The mean height of two features (A and B) was monitored, and swelling of the film was observed as Li^+ was inserted into the V_2O_5 host lattice. The degree of swelling can be calculated as the difference between the mean height of the sample at 2.44 V (point A or B) and the mean height at 1.80 V. This dimensional change can subsequently be correlated with the amount of charge passed during a charge/discharge cycle as well as the reversibility of the reaction. Future work will focus on such issues as inhomogeneities in the insertion process and how these inhomogeneities influence electrochemical characteristics.

This project is supported by ARO as part of a MURI (Grant: DAAH04-95-1-0095).

c. Particle Size Analysis of $LiCoO_2$

$LiCoO_2$ has emerged as the cathode material of choice for secondary lithium batteries. The powder processing route used to prepare this transition metal oxide intercalation compound is based on traditional solid-state reactions. Typically, this involves the mechanical mixing of oxides and/or carbonates followed by high temperature firing and extensive grinding of the resulting product to form micron-size particles. These synthesis conditions require long-range diffusion of the reactants and may result in inhomogeneities, abnormal grain growth and poor control of stoichiometry. While this method is useful for establishing basic properties, it generally produces micron-sized powders of variable chemical uniformity. In this program we are investigating the synthesis of secondary lithium battery cathode materials by use of the Pechini method, a solution processing approach based on a chelated solution formed by dissolving metal salts

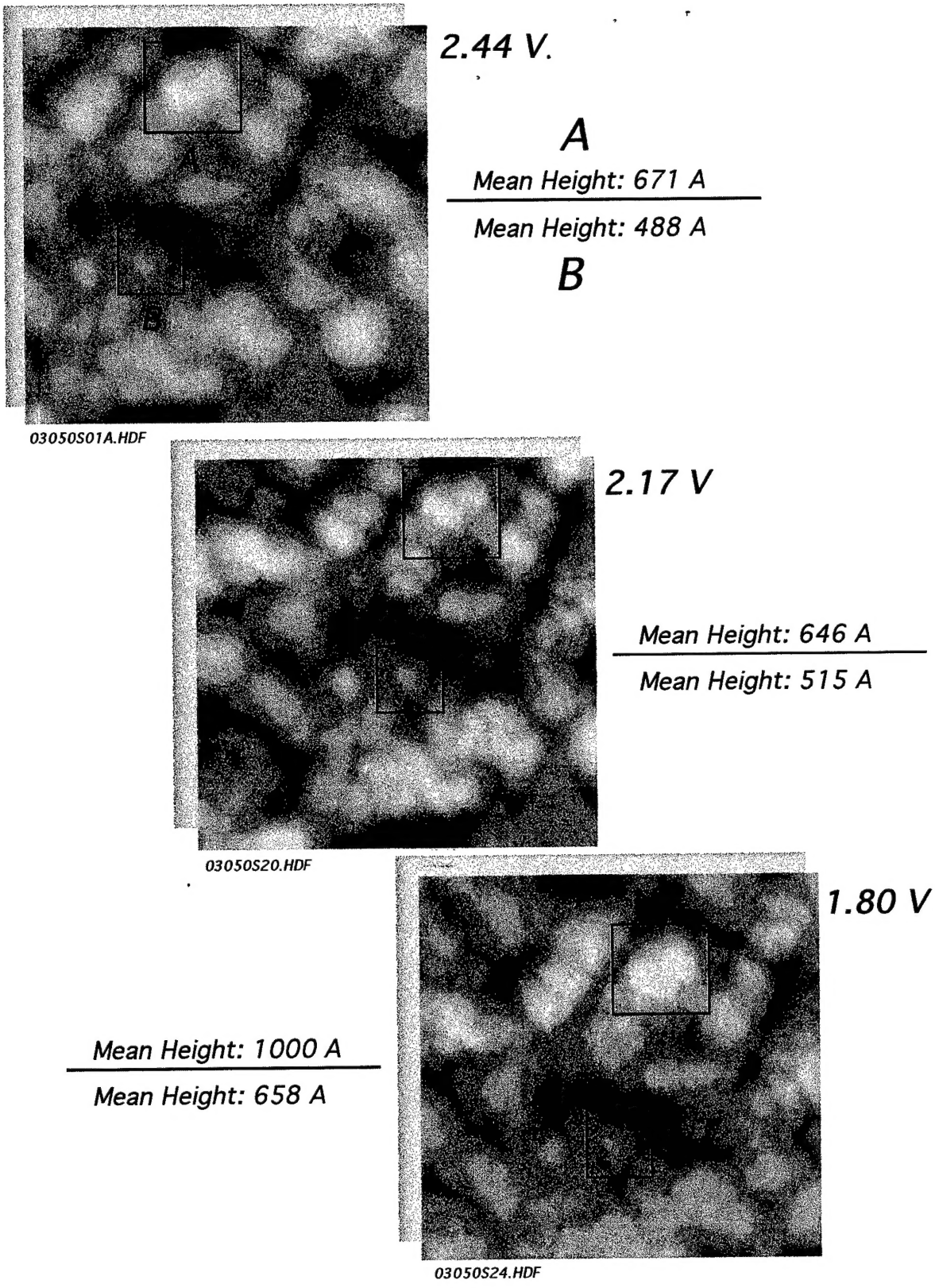

Figure 2 Lithium intercalation into vandium pentoxide xerogel cathode during discharge.

in a hydroxycarboxylic acid (citric acid). This approach is attractive for several reasons. The use of solution processing leads to molecular level mixing and highly uniform materials. Moreover, by minimizing the need for long-range diffusion of reactants, the lithium cobalt oxide phase forms at lower temperatures. This helps control the stoichiometry of the material by reducing potential problems associated with volatilization or disproportionation reactions as well as lead to the formation of nanometer-sized powders at substantially lower temperatures than can be achieved by solid-state methods.

We have used the Micromeritics Sedigraph 5100 to determine the particle size and particle size distribution of Pechini-processed materials heat treated to different temperatures. $LiCoO_2$ powders calcined at 300°C exhibit a size roughly in the 1 μm diameter range. With increasing calcining temperature, the particles start to coalesce forming larger particles. At 800°C, the measured particle size is roughly 10 μm. The large particles are believed to be agglomerates of small particles. The use of the Pechini method to prepare $LiCoO_2$ with variable crystallinity and powder morphology provides a novel opportunity in which to examine how these parameters influence electrochemical properties. The Pechini-processed powders heated to 800°C exhibit very good electrochemical performance. The lithium intercalation/deintercalation process is reversible and shows good capacity (≈ 150 mAh/g), corresponding to 0.53 moles Li. These characteristics are comparable to those of commerical $LiCoO_2$ powders.

This project was supported by the University of California MICRO program in connection with a grant from Hughes Aircraft.